

Tunnel ionization of open-shell atoms

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A generalized ADK (Ammosov-Delone-Krainov) theory for ionization of open shell atoms is compared to ionization experiments performed on the transition metal atoms V, Ni, Pd, Ta, and Nb. Our theory is found to be in good agreement for V, Ni, Pd, and Ta, whereas conventional ADK theory overestimates ionization by orders of magnitude. The key to understanding the observed ionization reduction is the angular momentum barrier. Our analysis shows that the determination of the angular momentum barrier in open shell atoms is nontrivial. The Stark shift is identified as the second dominant effect responsible for ionization suppression. Finally, these two effects cannot explain the Nb data. An analysis of the electron spins suggests that Pauli blocking might be responsible for the suppression of tunneling in Nb.

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Tunnel ionization theory was developed in several seminal works [1, 2]. All of these theories are based on the single active electron (SAE) approximation, where only the weakest bound electron interacts with the laser field. The most commonly used tunneling theories are ADK (Ammosov-Delone-Krainov) and MO-ADK (molecular-ADK) theory [2], which are in excellent agreement with experiments in noble gases and small molecules [3].

The situation is different for more complex systems. Theoretical predictions from ADK theory often overestimate experimentally measured ionization yields by orders of magnitude [4, 5]. Recently, a quasi-analytical multi-electron theory of tunnel ionization was developed [6], revealing that the SAE approximation loses its validity in complex materials. A comparison with ionization experiments in C₆₀ showed reasonable agreement. This theory opens the door to explore the new multi-electron physics associated with tunnel ionization in complex systems.

In this paper we develop the theory of Ref. [6] further to analyze tunnel ionization of the transition metal atoms Vanadium (V), Nickel (Ni), Palladium (Pd), Tantalum (Ta), and Niobium (Nb). They are significantly more complex than noble gas atoms due to an open *d* shell and large angular and spin momenta. ADK theory overestimates [5] ionization in transition metal atoms by orders of magnitude. Our work reveals the following new findings:

- (i) We find good agreement with V, Ni, Pd, and Ta experiments. This further corroborates the applicability of the theoretical framework, developed here and in Ref. [6], to general complex systems.
- (ii) The first major effect responsible for the suppression of ionization is found to be the angular momentum barrier. Due to the complexity of open shell atoms, determination of *l* is not as straightforward as in noble gases, but requires a careful analysis. This reveals unprecedented insight into the structure and complexity of transition metal atoms. The second dominant contribution to the suppression of tunneling comes from an increase of the

ionization potential caused by the Stark shift. Our analysis demonstrates the importance of the Stark shift for tunnel ionization.

- (iii) The two effects discussed in (ii) cannot explain the strong ionization reduction found in Nb. An analysis of the spins of *s*- and *d*-orbital electrons suggests that the reduction of tunnel ionization in Nb might be caused by Pauli blocking, an effect central to many-body physics.

- (iv) Starting from the quasi-analytical multi-electron theory of Ref. [6], a generalized multi-electron ADK/MO-ADK theory is derived, which includes correction factors accounting for multi-electron effects and angular momentum barrier.

Our analysis begins with the tunnel ionization rate in atomic units, as given in Ref. [6],

$$w_m = \frac{\Delta^{2(m+1)}}{(2\kappa)^{2|m|+1}|m|!} \left(\sum_l B_{lm} e^{-t} \right)^2, \quad (1)$$

where *l* and *m* refer to the angular momentum and magnetic quantum numbers of the field-free asymptotic wavefunction of the weakest bound valence electron that is matched with the wavefunction of the tunneling electron. In the case that *m* is a non-degenerate, good quantum number, e.g. homonuclear diatomic molecules, $w = w_m$, with *w* the ionization rate. When *m* is not a good quantum number, several *m* contribute to the tunneling wavefunction and $w = \sum_m w_m$. For *m* degenerate, e.g. noble gas atoms, the ionization rate is determined by $w = 1/(2l+1) \sum_m w_m$. Note that Eq. (1) corrects a misprint in Eq. (8) of Ref. [6] with respect to the position of \sum_l . Further, $B_{lm} = \sum_{m'} \mathcal{D}_{m'm}^l(\mathbf{R}) Q_{lm'} C_{lm'}$, and Q_{lm} is the normalization constant of the spherical harmonics [2, 6]. The rotation matrix $\mathcal{D}_{m'm}^l$ rotates the coordinate system by the Euler angle \mathbf{R} , and allows calculation of ionization along an arbitrary direction, once the matching coefficients C_{lm} have been determined along one direction. Finally, $t = \int_{z_0}^{z_1} p_z dz$, $1/\Delta^2 = \int_{z_0}^{z_1} 1/p_z dz$,

$p_z = \sqrt{\kappa^2 - 2zE + 2V(z)}$, and

$$V(z) = -\frac{Z}{z} + \frac{\beta_+ E}{z^2} - \frac{\beta_+}{2z^4} + \frac{l(l+1)}{2z^2}. \quad (2)$$

The electric field E is assumed to point along the z -direction, Z is the charge of the residual ion after ionization, and $\beta = \beta_n$ and $\beta_+ = \beta_{n-1}$ refer to the polarizability of the n -electron system before and after ionization [6]. The Stark shifted [7] and the field free ionization potential of the weakest bound electron are given by $\kappa^2/2 = I_p - (\beta - \beta_+)E^2/2$, and I_p , respectively. The four terms in Eq. (2) represent the barrier coming from the Coulomb potential, the laser polarization, the image charge, and the angular momentum, respectively. The last three terms are not accounted for in ADK/MO-ADK theory. Integration is performed between the limits z_0 and z_1 , where z_1 is the outer turning point.

The lower integration limit z_0 is the point at which the laser dressed, tunneling wavefunction is matched to the field free, asymptotic ground state, see Ref. [6]. Matching has to be done at a field free point. As complex systems are highly polarizable, the polarization field cancels the laser field at a point a , where $\beta_+ E/a^2 - aE \approx 0$. Solution of this equation gives $z_0 = a = \beta_+^{1/3}$. Due to shielding the inner part of the system, $z \leq a$, is approximately field free. In a metallic sphere, the matching point lies on the surface.

When $V(z) \ll \kappa^2/2$ for $z_0 < z < z_1$ is fulfilled, the square root in p_{z0} can be Taylor expanded. In this limit, all the integrals can be solved analytically and contact can be made between Eq. (1) and ADK/MO-ADK theory. The calculation is fairly involved; details will be given in a longer paper. The generalized ADK/MO-ADK ionization rate is given by

$$w_m = w_o \left(\frac{E}{2\kappa^2} \right)^\alpha \quad (3)$$

$$\alpha = \frac{l(l+1)E}{\kappa^3} + \frac{2\beta_+ E^2}{\kappa^3} - \frac{5\beta_+ E^3}{2\kappa^7}$$

where w_o refers to the conventional ADK/MO-ADK ionization rate,

$$w_o = \frac{|\hat{C}_{lm} Q_{lm}|^2}{2^{|m|} |m|! \kappa^{2Z/\kappa - 1}} \left(\frac{2\kappa^3}{E} \right)^{2Z/\kappa - |m| - 1} \exp\left(\frac{-2\kappa^3}{3E}\right). \quad (4)$$

The ADK/MO-ADK matching coefficient in Eq. (4) is related to the matching coefficient in Eq. (1) by $\hat{C}_{lm} = C_{lm} e^{\kappa z_0} z_0^{-Z/\kappa}$. We use here $w = 1/(2l+1) \sum_m w_m$. The three correction terms in α come from the angular momentum barrier, the laser polarization barrier, and the image charge term, respectively. The l -barrier is not contained in the ADK/MO-ADK theory. The l -dependence in ADK/MO-ADK theory comes from the spherical harmonics and the matching coefficient. In the limit of $l = 0$

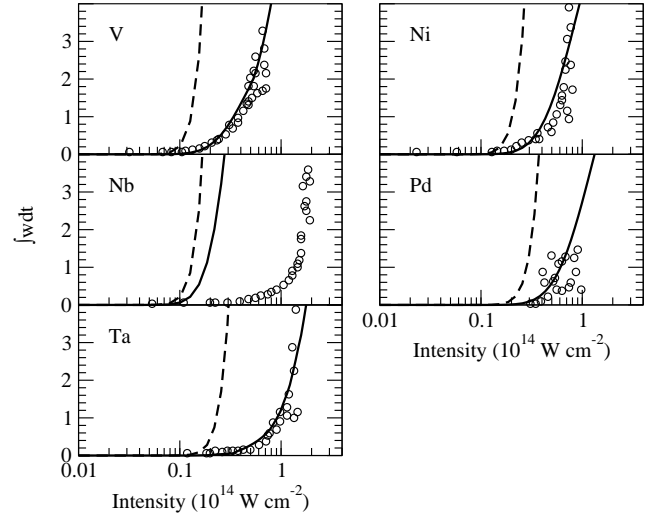


FIG. 1: Tunnel ionization yield $\int w dt$ in V, Ni, Nb, Pd, and Ta versus laser peak intensity. The open circles denote the experimental results from Ref. [5]. The dashed and full lines refer to the theoretical results obtained from ADK theory, and from our theory, Eq. (3), respectively. Gaussian laser pulse parameters: wavelength $1.5\mu\text{m}$ and FWHM width 50fs .

and small polarizability, Eq. (3) reduces to the conventional ADK/MO-ADK ionization rate, $w_m = w_o$. A comparison of Eq. (3) with Eq. (1) shows excellent agreement for the transition metal atoms investigated here. Therefore, we use Eqs. (3) - (4) throughout the paper. The applicability of (3) for complex molecules will be investigated in a future work.

Key to understanding tunnel ionization in transition metal atoms is knowledge of the angular momentum l of the asymptotic wavefunction of the weakest bound valence electron. Quantum chemistry codes have been used to determine l for small molecules and noble gas atoms [2, 8]. As Hartree-Fock (HF) is sufficient to model these systems, the asymptotic wavefunction can be obtained from the highest occupied molecular orbital. We find that this method is also applicable to Pd and gives $l = 2$, see the discussion below. This allows us also to extract \hat{C}_{lm} for Pd from the numerical analysis and to compare it with the ADK matching coefficient [2], as determined by quantum defect theory. The ADK matching coefficient is commonly used to calculate tunnel ionization of atoms. The numerical result is found to be by a factor of 1.2 smaller. This difference is insignificant and corroborates the validity of quantum defect theory. Hence, the ADK matching coefficient is used for all the other transition metal atoms, where a numerical determination is not possible.

In all other transition metals the wavefunction undergoes a complex configuration mixing, when the valence electron is pulled away from the nucleus to the asymptotic region. Quantum chemistry codes are not sensitive to the asymptotic part of the wavefunction, as they op-

timize the binding energy, which mainly depends on the wavefunction close to the nucleus. Although an accurate description of the asymptotic wavefunction is in principle possible within a configuration interaction (CI) analysis, in practice it requires an unreasonably large number of configurations. Therefore, due to the lack of proper numerical methods l is inferred from the configuration data given in table I.

Our analysis of the transition metal atoms starts with Vanadium. Whereas in noble gases l is determined by the highest occupied orbital, this is no longer possible here. Although the highest occupied orbital of V is a 4s orbital, the following more careful analysis of the total angular momentum L shows that $l = 0$ is forbidden. The total angular momentum of the atom and ion ground state is $L = 3$ and $L_+ = 2$, respectively, see table I. The plus subscript refers to ions and ion-parameters throughout the paper. From the angular momenta L and L_+ a range of possible values of l can be derived. This is done by using the field free, asymptotic, atomic ground state, which can be approximated as the tensor product of the ionic ground state and of the valence electron far away from the nucleus. As a result, the total angular momentum of the ion plus valence electron, as determined by the angular momentum addition theorem, has to be equal to the total angular momentum of the neutral atom. This is only possible when l fulfills the condition $L_+ - l \leq L \leq L_+ + l$, yielding $1 \leq l \leq 5$. The possible range of l can be further narrowed down by utilizing the fact that parity also has to be conserved. As V and V_+ have even parity, the parity of the asymptotic valence electron wavefunction must be even, too. This requires l to be even and thus, $l = 2, 4$. As the 3d orbitals are energetically close to the highest occupied 4s orbitals, the dominant tunneling channel comes from a 3d-orbital with $l = 2$.

We would like to note three points associated with the above analysis. First, the conservation laws were applied to the field free, asymptotic ground state, which is the initial state for tunneling. Angular momentum and parity are of course not conserved during tunnel ionization. Second, the atomic ground state close to the nucleus and in the asymptotic limit is described by different configurations. This mixing of configurations in the time independent ground state should not be confused with a time-dependent reconfiguration. Third, we assume that the atom relaxes adiabatically during ionization into its ionic ground state. When an excited state is populated after ionization, which is termed shake-up [9], the ionization potential increases by the energy difference between ion excited and ground state, ΔI . In transition metal atoms $\Delta I \approx 0.3 - 1\text{eV}$ is small, so that the shake-up channel might be important. Whereas it would be surprising when tunnel ionization leaves ions dominantly in an excited state, due to the complexity of the problem it also cannot be rigorously ruled out. Our angular momentum analysis gives $l = 0, 2$ for the shake-up channel.

In case $l = 2$, the shake up channel gives a small correction to the fundamental channel and our results remain unchanged. In case $l = 0$, our theory would predict a too large ionization yield, close to ADK theory. The $l = 0$ shake-up channel is excluded based on the fact that $l = 2$ explains the experimentally observed ionization suppression very well. We suggest an experiment to corroborate our conclusion. The first excited state in transition metal atoms is non-dipole allowed and therewith metastable. Therefore, the population of the ion states after ionization can be probed by exciting dipole allowed transitions and measuring fluorescence or the loss experienced by the probing laser. For example, in V_+ the lowest dipole allowed transitions from the $3d^4$ ground state and the first excited (metastable) $3d^34s$ state can be probed, with transition energies of $\approx 4.5\text{eV}$ and 4eV , respectively. In dependence on whether the shake-up channel has $l = 0$ or 2 , one would find a predominant population of the $3d^34s$ state or of the $3d^4$ ground state, respectively.

Given the simple approach used here and experimental uncertainties, our theory is in good agreement with the experimental data of Ref. [5]. In Fig. 1 the ionization yield $\int w[E(t)]dt$ is plotted versus the laser peak intensity. For pulse parameters and shape of the laser electric field $E(t)$ see the figure caption. Our theory (full line) explains the difference between experiment (empty circles) and ADK theory (dashed line). Half of the difference is due to the l -barrier which is not accounted for in ADK/MO-ADK theory. As β_+ is small, the role of the laser polarization induced barrier is insignificant. The other half of the difference is accounted for by the Stark shift, which reduces ionization by increasing the ionization potential. The large Stark effect arises from the big difference in polarizabilities β and β_+ , see table I. As the Stark effect increases with laser intensity, its effect is most pronounced at high intensities. Therefore, the ionization yield rises gradually and reproduces the shape of the experimental curve, in contrast to the abrupt rise predicted by ADK/MO-ADK theory. Switching off the l -barrier shows that the Stark effect requires the l -barrier to suppress ionization effectively. Without the l -barrier ionization would be shifted to lower intensities, where the role of the Stark effect is insignificant.

Part of the large discrepancy between ADK/MO-ADK theory and experiment might arise from the fact that ADK/MO-ADK overestimates tunnel ionization in the above barrier limit. The Coulomb barrier is suppressed at an electric field $E_{bs} = I_p^2/4$, which corresponds to a laser intensity of $7 \times 10^{12}\text{W/cm}^2$ in V. Hence, barrier suppression in V occurs before ADK/MO-ADK theory shows that significant ionization takes place. In H and He, ADK/MO-ADK theory overestimates above the barrier ionization rates by a factor of 2-4 [10], which is by far not enough to explain the difference in Fig. 1. In transition metals the magnitude of the overestimation is unknown. Nevertheless, we believe that barrier suppression

is not the dominant factor responsible for the difference between ADK/MO-ADK theory and experiment. Significant ionization usually takes place around the intensity at which the barrier is suppressed. In V ionization becomes dominant in the range between $4 \times 10^{13} \text{W/cm}^2$ and $7 \times 10^{13} \text{W/cm}^2$, which is by a factor of 5-10 larger than the barrier suppression intensity. It appears to be counterintuitive that ionization should only start at intensities so much higher than the barrier suppression intensity. In our opinion the large difference points to the fact that ADK/MO-ADK theory, which is exclusively based on the Coulomb barrier, underestimates the true tunneling barrier. This is corroborated by our theory, Eq. (2). Due to l -barrier and Stark shift, the tunneling barrier is not suppressed over the laser intensity range used in Fig. 1.

For Ni and Pd we get similarly good agreements as for V, see Fig. 1. For Ni our analysis yields $l = 2$. In Pd determination of l is straightforward. The total angular momentum changes from $L = 0$ to $L_+ = 2$. The configuration changes from $4d^{10}$ to $4d^9$, showing that the tunneling electron comes from a d-orbital and that $l = 2$, in agreement with the HF analysis discussed above.

In Ta it was not possible to unambiguously identify l . From table I we find two relevant ionization channels. The possible angular momentum values are $l = 0, 2, 4, 6$. Hence, ionization from an s-orbital and from a d-orbital are possible. In V tunneling from a d-orbital is preferred, probably because breaking of the closed subshell $4s^2$ configuration is energetically unfavorable. We suspect that tunneling from a d-orbital in Ta might be favored for similar reasons. This is supported by comparing theory and experiment for $l = 2$, which yields good agreement. For $l = 0$ the experimental data cannot be explained.

Finally, for Nb we could not get agreement with experimental data. The possible values of l are $l = 0, 2, 4$. Niobium does not have a closed s-subshell like V, Ni, and Ta, which might favor tunneling of a d-electron. Therefore, we use $l = 0$ in Fig. 1. We have also performed test calculations for $l = 2$ and 4. These also do not give satisfactory agreement, corroborating our conclusion that the l -barrier is not responsible for the observed ionization suppression. Further, ionization due to dimers and higher clusters was excluded experimentally [12].

A spin analysis of the s- and d-electrons shows that the spins of the tunneling and bound electrons are all parallel in Nb. In all other transition metal atoms the spins of the bound electrons are parallel, however the tunneling spin points in the opposite direction. Therefore, in V, Ni, Pa, and Ta, the exchange effect between tunneling and bound electrons is zero. In contrast to that, the tunneling electron in Nb feels the exchange effect with the bound electrons. The exchange effect makes it harder for the tunneling electron to pass the other open shell electrons and to escape. In the language of many-body physics this is termed Pauli blocking.

Based on the fact that none of the other mechanisms can explain the Nb experiments, we speculate that Pauli blocking is responsible for the observed ionization suppression. A quantitative proof will require a generalization of the current ionization theory to account for the exchange effect, which will be subject to future work.

Z	Neutral			Ion			Ip (eV)	l
	Conf.	$^{2S+1}L_J$	β	Conf.	$^{2S+1}L_J$	β_+		
V 23	$3d^3 4s^2$	$^4F_{\frac{3}{2}}$	12.4	$3d^4$	5D_0	3.1	6.75	2
Ni 28	$3d^8 4s^2$	3F_4	6.8	$3d^9$	$^2D_{\frac{5}{2}}$	1.4	7.64	2
Pd 46	$4d^{10}$	1S_0	4.8	$4d^9$	$^2D_{\frac{5}{2}}$	1.8	8.34	2
Ta 73	$5d^3 6s^2$	$^4F_{\frac{3}{2}}$	13.1	$5d^3 6s$	5F_1	7.7	7.89	2
Nb 41	$4d^4 5s$	$^6D_{\frac{1}{2}}$	15.7	$4d^4$	5D_0	4.7	6.76	0

TABLE I: Table for the transition metal elements V, Ni, Pd, Ta and Nb, containing the total charge of the nucleus, configuration, total spin and angular momentum, polarizability (\AA^3) of neutral and singly charged ion, ionization potential I_p and the angular momentum l of the tunneling electron. The plus subscript refers to singly charged ions and their properties throughout the paper. The polarizability is calculated by using density functional theory in the local density approximation [11]; β agrees with published data, see <http://webbook.nist.gov>; for β_+ no data is available for comparison. The configuration data is taken from <http://physics.nist.gov/PhysRefData/Handbook/index.html>.

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